

Disclaimer:

This English translation is produced by machine translation and may contain errors. The JPO, the INPIT, and those who drafted this document in the original language are not responsible for the result of the translation.

Notes:

1. Untranslatable words are replaced with asterisks (***).
2. Texts in the figures are not translated and shown as it is.

Translated: 23:53:24 JST 10/25/2010

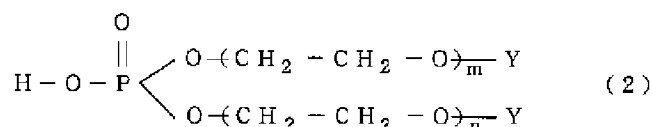
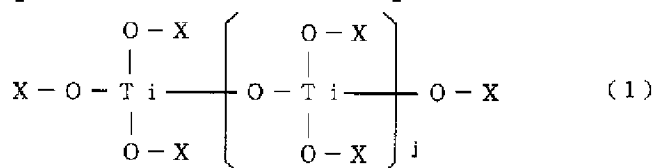
Dictionary: Last updated 10/08/2010 / Priority:

CLAIM + DETAILED DESCRIPTION

[Claim(s)]

[Claim 1] In a printer's ink constituent which mainly comprises paints, hydroxyl group content resin, a titanium system crosslinking agent, and an organic solvent, At least one sort (a ingredient) of a titanate compound as which said titanium system crosslinking agent is expressed in the following general formulas (1), [at least one sort (b ingredient) of JI (polyoxyethylene alkyl ether) phosphate denoted by a general formula (2)] a ingredient: A printer's ink constituent which is a reaction thing made to react at a rate that a rate of a molar ratio of b ingredient is set to :(0.5-4) 1, and is characterized by containing in 0.1 to 5weight % of the range of all the printer's ink composition.

[Chemical formula 1]



Here, as for the alkyl group of 3 to 18 or an acyl group, and Y, in a carbon number, a carbon number expresses the alkyl group of 1-18 independently X, respectively. j is an integer of 0-9, m and n are positive integers, and $m+n=2-10$ are filled.

[Claim 2]The printer's ink constituent according to claim 1 using polyamide resin and/or a cellulose derivative as said hydroxyl group content resin.

[Claim 3]The printer's ink constituent according to claim 1 using polyurethane resin as said hydroxyl group content resin.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]About a solvent type printer's ink constituent, in more detail, this invention has the outstanding adhesiveness, heat resistance, and oil resistance, and relates to a solvent type printer's ink constituent with good preservation stability in temporality.

[0002]

[Description of the Prior Art]As binder resin of the various printer's ink for plastic films, polyamide resin and a cellulose derivative are used well.

[0003]For example, although ink is printed only on the front side of a covering object and the thing of the easy composition (called a front printing printing method) of not printing is used for the bag of confectionery or rice on the back side in contact with foodstuffs, Typical binder resin of this printer's ink for front printing is generally an

independent system of polyamide resin, or a combined use system with a cellulose derivative.

[0004]This is because the performances required of the printer's ink for front printing are mainly gloss, adhesiveness, heat resistance, oil resistance, etc., and, as for polyamide resin, gloss and adhesiveness, and a cellulose derivative give heat resistance to ink.

[0005]There is a tendency for heat resistance sufficient by the independent system of polyamide resin not to be obtained, and for the adhesiveness over the gloss and the various films of ink to fall by a combined use system with a cellulose derivative, and However, heat resistance high only by these systems, It is difficult to obtain gloss and the ink composition with which it is simultaneously satisfied of adhesiveness.

[0006]Therefore, although the method of adding alkyl titanate as a crosslinking agent during ink composition is known as a method of raising these demand performance, there is a problem of yellowing of ink and the preservation stability in temporality falling.

[0007]Although he has proposed the method of adding titanium stearate as a crosslinking agent by Tokuganhei7-183039, applicant of this application has the problem that the oil resistance of the printer's ink constituent obtained becomes insufficient, when the content of a crosslinking agent increases.

[0008]Although the system which added the reaction thing with titanium ORUSO ester, phosphoric acid monoalkyl, or phosphoric acid JIARUKIRU is also proposed by JP,S61-37851,A, In these systems, in order to acquire sufficient effect, the content of a crosslinking agent increases, and it has the problem that the preservation stability in temporality falls.

[0009]Although the thing of composition (called a back printing printing method) of the packaging bag of the food packing use of which high definition is required, or a boil retort use printing ink at the back of a covering object on the other hand, and also laminating a film in a printing surface is used, Typical binder resin of this printer's ink for back printing is generally polyurethane resin. Although this is because the performance required of the printer's ink for back printing is heat resistance, heat-resistant water, etc. which paste up with a film mainly extensive type and are equal to lamination intensity or boil retorting, it is difficult to be satisfied with a polyurethane resin independent system of such performances.

[0010]Although the method proposed by aforementioned JP,S61-37851,A also for this problem solving can be used, that effect is still insufficient.

[0011]

[Problem to be solved by the invention]Then, there is SUBJECT of this invention in the ink film which has good adhesiveness, heat resistance, and oil resistance being obtained when printed by various plastic films, and also providing a printer's ink constituent with good preservation stability in temporality.

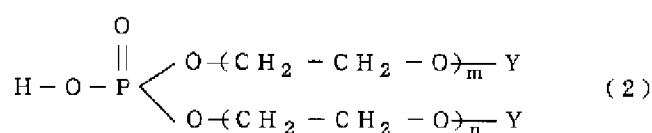
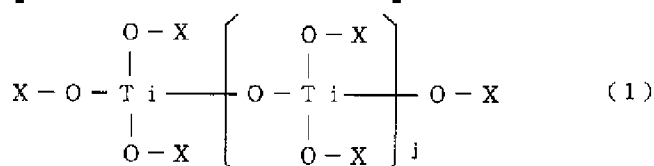
[0012]

[Means for solving problem]Namely, in the printer's ink constituent in which this invention mainly comprises paints, hydroxyl group content resin, a titanium system crosslinking agent, and an organic solvent, At least one sort (a ingredient) of the titanate compound as which said titanium system crosslinking agent is expressed in the following general formulas (1), [at least one sort (b ingredient) of JI (polyoxyethylene alkyl ether) phosphate denoted by a general formula

(2)] a ingredient: It is the reaction thing made to react at a rate that the rate of a molar ratio of b ingredient is set to : (0.5-4) 1, and is related with the printer's ink constituent containing in 0.1 to 5weight % of the range of all the printer's ink composition.

[0013]

[Chemical formula 2]



[0014]Here, as for the alkyl group of 3 to 18 or an acyl group, and Y, in a carbon number, a carbon number expresses the alkyl group of 1-18 independently X, respectively. j is an integer of 0-9, m and n are positive integers, and m+n=2 - 10 are filled.

[0015]This invention relates to the printer's ink constituent which uses polyamide resin and/or a cellulose derivative as said hydroxyl group content resin.

[0016]This invention relates to the printer's ink constituent which uses polyurethane resin as said hydroxyl group content resin.

[0017]

[Mode for carrying out the invention]Hereafter, it explains in more detail about this invention.

[0018]<Paints> As paints used with the ink composition of this invention, the inorganic matter, organic color, or constitution paints which can generally be used with an organic-solvent type ink

composition can be used first.

[0019]As an inorganic pigment, specifically, [titanium oxide, red ocher, antimony red cadmium red, cadmium yellow, cobalt blue, Prussian blue ultramarine, carbon black, black lead, etc.] [as an organic color] Soluble azo pigment, insoluble azo pigment, an azo lake color, a condensation azo pigment, a copper phthalocyanine pigment, condensed multi-ring paints, etc. can be mentioned.

[0020]As constitution paints, calcium carbonate, kaolin, clay, barium sulfate, aluminium hydroxide, talc, etc. can be mentioned.

[0021]The content in the inside of the ink composition of these paints is usually about 1 to 50 weight %.

[0022]The binder resin used with the ink composition of <binder resin> this invention is hydroxyl group content resin, is mainly a polyamide cellulose derivative mixture system or a polyurethane system, and can add other resin if needed.

[0023]-, [polyamide resin usable as binder resin of the ink composition of polyamide resin this invention] The acid ingredient which may mainly contain a part of polymerization fatty acid and also a fatty series, alicycle fellows and aromatic dicarboxylic acid, and fatty series monocarboxylic acid, The amine ingredient which a fatty series, alicycle fellows, a perfume fatty series, and aromatic series polyamine may mainly be independent, or may contain a part of mixture and also first class, and the second class monoamine is made to react.

[0024]Here, generally a carbon number is obtained by the unsaturated fatty acid of 16 to 22, or the polymerization of the ester, and polymerization fatty acid contains monobasic fatty acid, dimerization polymerization fatty acid, 3 quantification polymerization fatty acid, etc.

[0025]As fatty series dicarboxylic acid, cyclohexanedicarboxylic acid

etc. can be mentioned as alicyclic dicarboxylic acid, such as succinic acid, adipic acid, azelaic acid, and maleic acid, and isophthalic acid, terephthalic acid, etc. can be mentioned as aromatic dicarboxylic acid.

[0026]As fatty series monocarboxylic acid, acetic acid, stearic acid, oleic acid, linoleic acid, etc. can be mentioned.

[0027]On the other hand as an amine ingredient, as polyamine, ethylene diamine, Fatty series Diamine, such as propylene diamine and hexamethylenediamine, Fatty series polyamine, such as diethylene triamine and bird ethylene tetramine, [as aromatic diamine, such as perfume fatty series Diamine, such as alicyclic diamine, such as cyclohexyl diamine and ISOHO diamine, and KISHIRI diamine, Feni diamine and JIAMINO diphenyl methane, the first class, and the second class monoamine] Monod, such as Monod, such as a butylamine, octylamine, and JIECHIRU amine, and G alkylamine, monoethanolamine, mono-propanolamine, JIETANORU amine, and dipropanolamine, and G alkanol amine can be mentioned.

[0028]When using only especially polyamide resin as binder resin of ink, in order to give reactivity with a crosslinking agent, as the first class or the second class monoamine ingredient, alkanol amine is used and the polyamide resin which has a hydroxyl group is used in the molecule whose hydroxyl value is 0.5 to about ten. In this case, the polyamide resin which does not contain a hydroxyl group may be used together.

[0029][as a method of compounding polyamide resin from the above acid ingredient and amine ingredient] It is desirable 0.9/1.0-1.0/0.9, and to consider it as 1.0/1.0 preferably, and to make 160-280 °C of reaction temperature the ratio of the carboxyl group/amino group of a

reaction ingredient react under decompression of about 100 torr in the final stage as 180-230 °C preferably.

[0030]-, [as a cellulose derivative usable as binder resin of the ink composition of cellulose derivative this invention] Methyl cellulose, ethyl cellulose, etc. can be mentioned as nitroglycerine cellulose and a low-grade acyl group substitution object as a nitro group substitution object as low-grade alkyl-group substitution objects, such as cellulose acetate and cellulose acetate propionate.

[0031]Although the thing of the range used with a usual paint and ink composition can also use this invention convenient, [the molecular weight of these cellulose derivatives, the degree of substitution of a hydroxyl group, etc.] Use of the nitro group substitution object from the heat-resistant field where that whose degree of substitution of a hydroxyl group is 1.3 to about 2.7 is preferred is advantageous, and from an adhesive field, since the low-grade acyl group substitution object and the low-grade alkyl-group substitution object are advantageous, it is preferred to use it, choosing suitably according to the purpose of use.

[0032]In this invention, the amount of the polyamide resin system binder resin used usually has 5 to 30weight % of a range preferred from viscosity or a fluid field in an ink composition. When it is considered as polyamide resin-cellulose derivative system binder resin, [a binder resin total amount] Usually, it is about 5 to 30 weight %, and the range of 1.0 / 0.1 - 1.0/0.5 (wt. ratio) is preferred from viscosity or a fluid field to in an ink composition from gloss or a heat-resistant field as a combined use ratio of polyamide resin/cellulose derivative. In the case of polyamide resin-cellulose derivative system binder resin, what does not contain a hydroxyl group as polyamide

resin is usable.

[0033]-, [polyurethane resin usable as binder resin of the ink composition of polyurethane resin this invention] It is polyurethane resin which compounds urethane pre polymer by the reaction of an organic diisocyanate compound and a polymer diol compound, makes a chain extension agent and a reaction stop agent react, and is obtained.

[0034]First, [as an organic diisocyanate compound] Aromatic series diisocyanate compounds, such as tolylene diisocyanate, 1, 4-cyclohexane diisocyanate, Perfume fatty series diisocyanate compounds, such as fatty series diisocyanate compound [, such as alicycle fellows diisocyanate compounds, such as isophorone diisocyanate, and hexamethylene di-isocyanate] and alpha, alpha, alpha', and alpha'-tetramethyl xylylene diisocyanate, are mentioned.

[0035]Although it can be used these organic diisocyanate compounds being able to be independent, or mixing, the thing of the alicycle fellows from the field of solubility and the mobility of ink, a fatty series, or a perfume fatty series is preferred.

[0036]As a polymer diol compound, various polymer diol compounds besides a polyether diol compound and a polyester diol compound can be used.

[0037]Here, as a polyether diol compound, alkylene oxide additions, such as polyalkylene glycols, such as polyethylene glycols and polypropylene glycol, an ethylene oxide of bisphenol A, and propylene oxide, can be mentioned.

[0038][as a polyester diol compound] What is produced by making carry out the condensation reaction of dibasic acid, such as adipic acid, sebacic acid, and anhydrous FUTARU acid, and the glycols, such

as ethylene glycol, propylene glycol, 1, 4-butanediol, neopentyl glycol, and 3-methyl 1,5-pentanediol, can mention.

[0039]Polycaprolactone JIORU, polycarbonate JIORU, poly butadiene JIORU, etc. can be mentioned as other polymer diol compounds.

[0040]As these polymer JIORU, the thing of 300-6000 has a preferred number average molecular weight. Although it can be used said polymer JIORU being able to be independent or mixing, the lamination intensity of the lamination ink obtained and the field of boil retort aptitude to a polyester diol compound is more preferred.

[0041]The equivalent ratio of an isocyanate group and a hydroxyl group of the operating ratio of said organic diisocyanate compound and a polymer diol compound is usually $:(1.3-3.0) \ 1.0$ and a range more preferably set to $:(1.5-2.0) \ 1.0$.

[0042]Next, as a chain extension agent, the poly alcoholic compound which first has two hydroxyl groups of the 1st class, such as the Gia Minot alcoholization ****, such as aminoethylethanolamine for introducing a hydroxyl group in a polyurethane molecule, and glycerin, and one or more hydroxyl groups of the 2nd class can be used.

[0043]When introducing a hydroxyl group in a molecule by the after-mentioned reaction stop agent, a diol compound or a diamine compound can be used.

[0044]As a diol compound here Ethylene glycol, propylene glycol, Can mention 1, 4-butanediol, neopentyl glycol, 1, and 6-hexandiol etc., and, [as a diamine compound] Ethylene diamine, propylene diamine, hexamethylenediamine, alpha, alpha, alpha', and alpha'-tetramethyl KISHIRI range amine, ISOHO lounge amine, etc. can be mentioned.

[0045]In order [next,] to introduce a hydroxyl group in a polyurethane molecule as a reaction stop agent, Can use the compound which has

both functional groups reacted to a hydroxyl group and isocyanate groups, such as monoethanolamine and JIETANORU amine, and, [0.5 Eq or less of the residual isocyanate group before a reaction stop] Monoalcohol compounds, such as monoamine compounds, such as monobutyl amine, methanol, ethanol, can be used together.

[0046]When the hydroxyl group is introduced in the molecule using the chain extension agent, monoamine and monoalcohol can be used alone.

[0047]As a method of manufacturing polyurethane resin from each above material, the publicly known method for manufacturing polyurethane resin for ink binders can use as it is.

[0048]It is preferred to introduce a hydroxyl group into polyurethane resin by the above-mentioned method, and to use polyurethane resin whose hydroxyl value is 0.5 to about 30.

[0049]moreover -- as the number average molecular weight of said polyurethane resin -- usually -- 5,000 thru/or 150,000 -- it is 30,000 thru/or 100,000 more preferably.

[0050]In this invention, the usual amount of the polyurethane resin system binder used has 5 to 30weight % of a preferred range in an ink composition from viscosity or a fluid field.

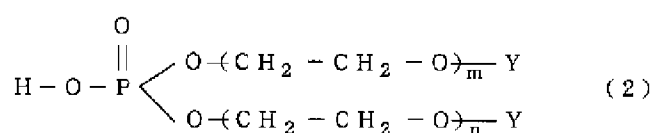
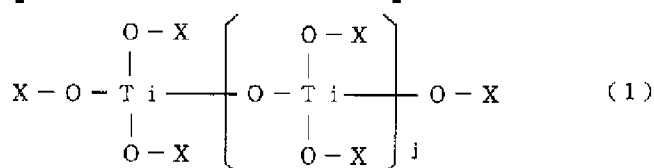
[0051]- As other binder resin and other binder resin, the various binder resin used with the solvent type printer's ink for films can be used, and maleic acid system resin, an acrylic resin, polyester resin, terpene resin, petroleum resin, ketone resin, etc. can specifically be mentioned. The amount used in the ink composition of these binder resin is usually about 0 to 10 weight %.

[0052][<titanium system crosslinking agent> this invention] [an usable titanium system crosslinking agent] It is a reaction thing

produced by making at least one sort (a ingredient) of a titanate compound denoted by the following general formula (1), and at least one sort (b ingredient) of JI (polyoxyethylene alkyl ether) phosphate denoted by a general formula (2) react.

[0053]

[Chemical formula 3]



[0054]Here, as for an alkyl group of 3 to 18 or an acyl group, and Y, in a carbon number, a carbon number expresses an alkyl group of 1-18 independently X, respectively. j is an integer of 0-9, m and n are positive integers, and m+n=2 - 10 are filled.

[0055]The oil resistance of printer's ink which will be obtained if a carbon number of an alkyl group of X and an acyl group exceeds 18 in molecular structure denoted by a general formula (1) falls, the heat resistance of printer's ink which will be obtained on the other hand if there are few carbon numbers than three falls, and it is not desirable. If j exceeds 9, the heat resistance of printer's ink obtained will fall.

[0056][as an alkyl group of the carbon numbers 3-18 denoted by X]

For example, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-hexyl, n-octyl, 2-ethylhexyl, DESHIRU, DODESHIRU, tetradecyl, octadecyl, etc. are raised. As an acyl group of the carbon numbers 3-18 denoted by X, pro PIONIRU, BUCHIRIRU, HEKISA noil, octanoyl,

decanoyl one, lauroyl one, tetra-decanoyl, stearyl, etc. are raised.

[0057]The titanate compound which contains the acyl group of the carbon numbers 8-18, such as octanoyl, decanoyl one, lauroyl ones, tetra-decanoyl, and stearyl, from the point which makes heat resistance of the printer's ink obtained good in the titanium atom in a molecule and more than the same number is preferred.

[0058]As an example of a ingredient, tetraisopropoxy titanium, tetra-n-butoxytitanium, Tetrakis (2-ethylhexyloxy) titanium, tetrastearoyloxy titanium, Triisopropoxy titanium monostearate, tree n-butoxytitanium monostearate, Diisopropoxytitanium distearate, G n-butoxytitanium distearate, bis(2-ethylhexyloxy)titanium distearate, and its polymer of 2-10 ($j=1-9$) can be mentioned. These titanate compounds are independent, or can mix and use two or more sorts.

[0059]The titanium stearate system compound which has a stearyl machine with an alkyl group as a titanate compound from the heat-resistant field of ink as a basis denoted by X of a general formula (1) can use it more conveniently.

[0060]In the molecular structure denoted by a general formula (2), a hydroxyl group is a reactive site to the compound denoted by a general formula (1), it is required in order to acquire the effect of this invention, but if it becomes these two or more bases, the preservation stability of an ink composition will fall. A manufacture top is difficult for the compound in which the carbon number of the alkyl group denoted by Y exceeds 18, and it is not suitable for use. The heat resistance of the printer's ink which will be obtained if the fall of preservation stability is seen by less than two and the value of $m+n$ exceeds 10 falls.

[0061]The carbon number denoted by Y is raised, for example for methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, DODESHIRU,

octadecyl, etc. as an alkyl group of 1-18.

[0062]As an example of b ingredient, it is JI. [POE(2) propyl ether] Phosphoric acid, JI [POE (2) butyl ether] Phosphoric acid, JI [POE(4) propyl ether] Phosphoric acid, JI [POE (4) butyl ether] Phosphoric acid, JI [POE(4) hexyl ether] Phosphoric acid, JI [POE(4) octyl ether] Phosphoric acid, JI [POE (4) dodecylether] Phosphoric acid, JI [POE (4) octadecyl ether] Phosphoric acid, JI [POE(6) propyl ether] Phosphoric acid, JI [POE (6) butyl ether] Phosphoric acid, JI [POE(8) propyl ether] Phosphoric acid, JI [POE (8) butyl ether] Phosphoric acid, JI [POE(10) propyl ether] Phosphoric acid, JI [POE (10) butyl ether] Phosphoric acid etc. can be mentioned. These JI (polyoxyethylene alkyl ether) phosphate is independent, or can mix and use two or more sorts. In the above, POE refers to polyoxy ethylene, and the inside of () expresses the number of addition Mol.

[0063]The reaction ratio of a ingredient and b ingredient is a rate (rate of a molar ratio) used as a ingredient:b ingredient =(0.5-4):1, and if the heat resistance of ink will fall if a ingredient becomes less than the aforementioned range, and it increases on the other hand, the preservation stability of ink falls and it is not still more preferred.

[0064]The reaction of a ingredient and b ingredient can be performed carrying out dropping mixture of the b ingredient solution gradually into a ingredient solution usually dissolving each ingredient in the organic solvent of alcoholic solvent, ketone solvent, etc. which can be dissolved, and cooling to room temperature or less than it.

[0065]The content of the titanium system crosslinking agent produced by making it above is 0.1 to 5 weight % to the All Printing Bureau Labour Union ink composition. If the content of a titanium system crosslinking agent becomes less than the aforementioned range, and

sufficient heat resistance and oil resistance will not be acquired and will increase, the preservation stability of ink will fall.

[0066][as an organic solvent used by <organic-solvent> this invention] Aromatic hydrocarbon systems, such as toluene and xylene, acetone, methyl ethyl ketone, Ketone systems, such as methyl isobutyl ketone, acetic acid methyl, ethyl acetate, propyl acetate, Various organic solvents, such as glycol systems, such as alcohol systems, such as ester systems, such as butyl acetate, methanol, ethanol, and propanol, and ethylene glycol, and propylene glycol, and a derivative of those, can be mentioned, and it is usually used as a partially aromatic solvent.

[0067][as a method of manufacturing the ink composition of this invention using the material more than <the manufacturing method of ink>] The method of milling mixtures, such as a pigment agent, using a high-speed mixer, a ball mill, SANDOMIRU, attritor, etc. binder resin, paints, the organic solvent, and if needed, and also adding the remainder of a predetermined material and mixing is common.

[0068]The ink composition of <use> this invention can mainly be printed on various covering objects using a gravure printing method.

[0069]Here, [as a covering object in which an ink composition is printed] The usual extension polypropylene (OPP) film, an unextended polypropylene (CPP) film, Polyester films, such as a denaturation polypropylene film and a polyethylene terephthalate (PET) film, The extension polypropylene (VM-OPP) film in which metal other than various plastic films, such as nylon and polystyrene, such as aluminum, was vapor-deposited, respectively, an unextended polypropylene (VM-CPP) film, a polyethylene terephthalate (VM-PET) film, etc. are raised.

[0070][the system which uses polyurethane resin as a binder of ink]
After being printed by the above-mentioned film, to a printing surface
An imine system, an isocyanate system, Anchor coat agents, such as
a polybutadiene system and a titanium system, are coated, adhesives,
such as a urethane system, are coated to the extrusion lamination
which laminates melting polyolefin, and a printing surface, and it can
use also for the dry lamination which laminates a plastic film.

[0071]The printer's ink constituent of this invention demonstrates the
outstanding effect which is not in the conventional ink composition not
only to the usual plastic film but to a metal vapor deposition film.

[0072]

[Working example]Hereafter, although an embodiment explains this
invention more concretely, this invention is not limited to this. A part
and especially % express weight section and weight %, as long as
there is no limitation.

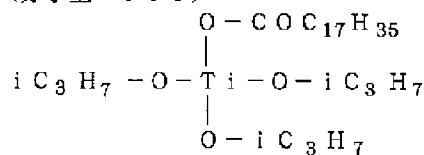
[0073]The titanate compound and JI (polyoxyethylene alkyl ether)
phosphate which were used in the example of the <manufacture of
titanium system crosslinking agent> following manufacture are as
follows.

[0074]

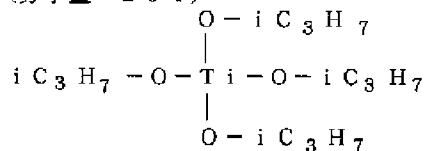
[Chemical formula 4]

チタネート化合物

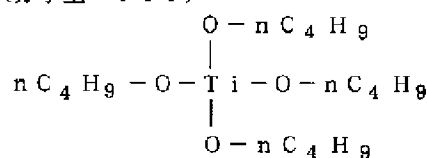
化合物 T 1 (分子量 508)



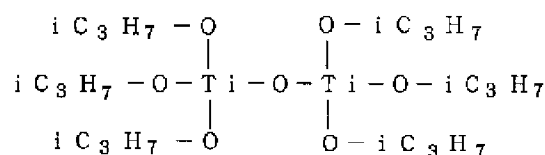
化合物 T 2 (分子量 284)



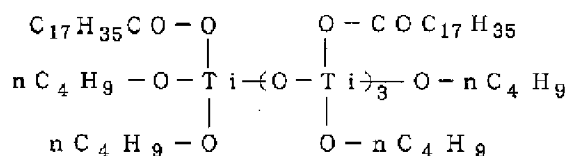
化合物 T 3 (分子量 340)



化合物 T 4 (分子量 466)



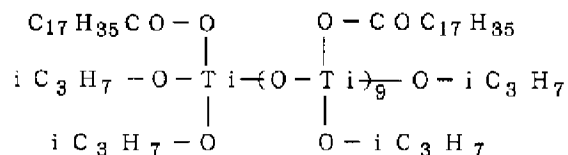
化合物 T 5 (分子量 1810)



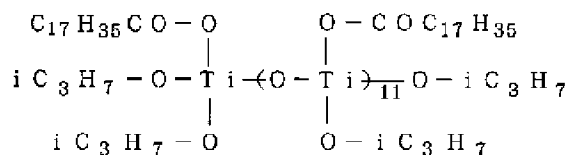
[0075]

[Chemical formula 5]

化合物 T 6 (分子量 4162)



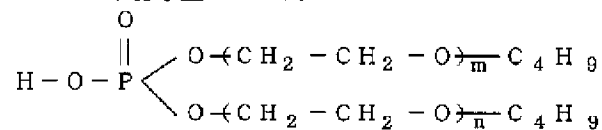
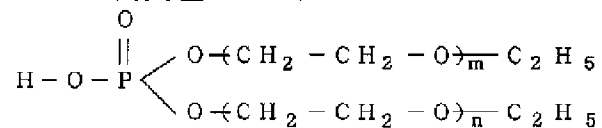
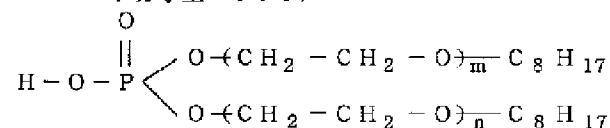
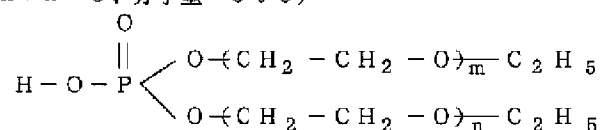
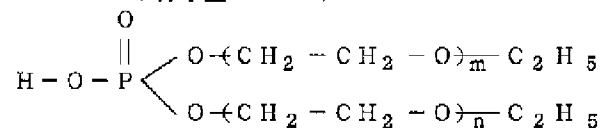
化合物 T 7 (分子量 4974)



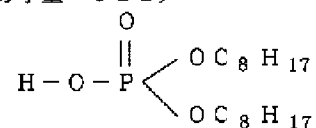
[0076]

[Chemical formula 6]

ジ（ポリオキシエチレンアルキルエーテル）フォスフェート

化合物 P 1（ $m + n = 2$ 、分子量 298）化合物 P 2（ $m + n = 4$ 、分子量 330）化合物 P 3（ $m + n = 6$ 、分子量 586）化合物 P 4（ $m + n = 8$ 、分子量 506）化合物 P 5（ $m + n = 10$ 、分子量 594）

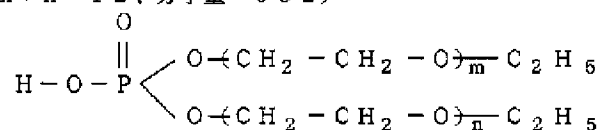
化合物 P 6（分子量 322）



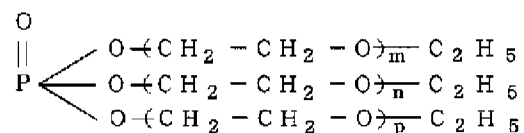
[0077]

[Chemical formula 7]

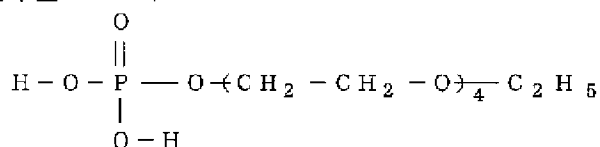
化合物 P 7 (m + n = 12、分子量 682)



化合物 P 8 (m + n + p = 4、分子量 358)



化合物 P 9 (分子量 292)



[0078]Preparing 677 copies of 75% isopropanol solution of the compound T1 in the reaction machine provided with example of manufacture 1 stirrer, the condenser tube, and the dropping funnel, cooling a reaction machine with a cooling trough, and keeping an internal temperature at 5-10 **.Were dropped, and carry out churning mixture, 355 copies of 75% isopropanol solution of the compound P1 was made to let a dropping funnel pass and to react gradually, and titanium system crosslinking agent No.1 was obtained.

[0079]By the same operation as the example 2 of manufacture - the example 1 of 19 manufactures, titanium system crosslinking agent No.2 - 19 were obtained according to combination of Table 1.

[0080]

[Table 1]

表 1

			チタン系架橋剤 7.5% IPA 溶液 No.																				
			1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19		
チタネート 化合物の 7.5% IPA溶液	チタネート 化合物	No.	T1							T2	T3	T4	T5	T6	T1							T7	
		含有量 (部)	508							284	340	466	1890	4178	508							4990	
		IPA含有量 (部)	169							95	113	155	630	1393	169							1663	
DPOEAEF 化合物の 7.5% IPA溶液	DPOEAEF 化合物	No.	P1			P2	P3	P4	P5	P1							P6	P7	P8	P9	P1		
		含有量 (部)	266	298	80	330	586	506	594	298							630	70	322	682	358	292	298
		IPA含有量 (部)	89	99	27	110	185	167	198	99							210	23	107	227	119	97	99

DPOEAEF 化合物：ジ（ポリオキシエチレンアルキルエーテル）フォスフェート IPA：イソプロパノール

[0081]300 copies of commercial polyamide resin (REOMAIDO S2600, KAO CORPORATION make) was dissolved into 280 copies of <manufacture of polyamide resin varnish> toluene, 280 copies of methyl ethyl ketone, and the partially aromatic solvent of 140 copies of isopropanols, and the polyamide (PA) resin varnish of 30% of solid content was obtained.

[0082]The soluble cotton HIG1/2 (made by ASAHI KASEI KABUSHIKI KAISHA) 150 copy was dissolved in 850 copies of <manufacture of cellulose derivative varnish> ethyl acetate as nitroglycerine cellulose, and the cellulose derivative (CN) varnish of 15% of solid content was obtained.

[0083]To the same device as the example 1 of <manufacture of polyurethane resin varnish> composition, 39.1 copies of isophorone diisocyanate, 207 copies of polybutylene adipate diol of the number average molecular weight 2000 compounded from adipic acid and 1 and 4-butanediol is taught, and it was made to react at 100 ** for 10 hours, introducing nitrogen gas. After cooling, add 193 copies of toluene, and 193 copies of methyl ethyl ketone, and it dissolves

uniformly, Added 193 copies of isopropyl alcohol, and 11.9 copies of ISOHO lounge amine, and it was made to react for 20 minutes, and also the reaction was stopped by 1.3 copies of monoethanolamines, and the polyurethane (PU) resin varnish of the number average molecular weight 25000 and 30% of solid content was obtained.

[0084]According to combination of the one to Embodiments 1-20 and comparative example 16 tables 2 and 3, the resinous principle and partially aromatic solvent of paints and a proper quantity were prepared, and it kneaded for 30 minutes with the red devil type paint conditioner, and also addition mixture of the remaining ingredients was carried out, and the ink composition of Embodiments 1-20 and the comparative examples 1-16 was prepared.

[0085]Titanium oxide (TIPAQUE R-900, E. I. du Pont de Nemours & Co. make) was used as paints. The thing of composition of toluene / methyl-ethyl-ketone / isopropyl alcohol =40/40/20 weight ratio was used as a partially aromatic solvent.

[0086]In accordance with the valuation method below a <evaluation test>, the oil resistance of the ink composition of Embodiments 1-20 and the comparative examples 1-16, heat resistance, adhesiveness, and viscosity stability with the passage of time were evaluated, and the result was shown in Tables 2 and 3.

[0087][the ink composition using polyamide resin/cellulose derivative] It is used in the field which needs heat resistance and oil resistance especially for an OPP film use, and the ink composition using polyurethane resin is used in the field which seldom needs heat resistance and oil resistance for various plastic films. Then, the performance needed for ink, respectively estimated.

[0088](Adhesiveness)

Valuation method Each examination ink containing polyamide resin/cellulose derivative was printed and dried by warm air on the OPP film with the photogravure proofreading machine, and printed matter was obtained. Each examination ink containing polyurethane resin was printed and dried by warm air on the OPP film, the PET film, and the aluminum vapor deposition PET film with the photogravure proofreading machine, and printed matter was obtained. In the case of the aluminum vapor deposition PET film, it printed to the aluminum vapor deposition side. The cellophane tape was stuck on the printing surface of these printed matter, and the printing coat when removed quickly evaluated adhesiveness from the degree which exfoliates from a film.

[0089]

Valuation-basis A: A printing coat does not exfoliate at all from a film.

B: As a rate of surface ratio of a printing coat, less than 20% exfoliates from a film. It carries out.

C: As a rate of surface ratio of a printing coat, not less than 20% and less than 50% are Phi. It exfoliates from RUMU.

D: As a rate of surface ratio of a printing coat, not less than 50% exfoliates from a film.

[0090](Heat resistance)

Valuation method Aluminum foil was pressed for 2 seconds by the pressure of 1.6 kg/cm^2 using the heat-sealing testing machine which equipped the printing surface which printed each examination ink containing polyamide resin/cellulose derivative on the OPP film with the photogravure proofreading machine with the heat board which has an 80-160 °C heat inclination. The heat resistance of examination ink

was evaluated from the minimum temperature which the ink of a printing surface transfers to aluminum foil.

[0091]

評価基準 A : 160℃以上のもの
 B : 140℃以上、160℃未満のもの
 C : 120℃以上、140℃未満のもの
 D : 100℃以上、120℃未満のもの
 E : 100℃未満のもの

[0092](Oil resistance)

Valuation method The printing surface which printed each examination ink containing polyamide resin/cellulose derivative on the OPP film with the photogravure proofreading machine was rubbed 100 times under 500 g of load with the reliance cloth into which vegetable oil was infiltrated using the frictional testing machine-proof [Gakushin-type], and oil resistance was evaluated from change of the printing surface.

[0093]

Valuation-basis A: A printing surface and a reliance cloth have no change.

B: Although it is changeless to a printing surface, a reliance cloth colors.

C: A line-like crack is found in a printing surface.

D: A field-like crack is found in a printing surface.

[0094](Viscosity stability with the passage of time) passing for seven days at 40 ** of valuation method examination ink from the viscosity change (ink viscosity measurement data in 30 rpm of a B-type-viscosity meter) before and behind temporality -- the time -- viscosity stability -- it evaluated.

[0095]

Valuation-basis A: In the viscosity ratio thing C:temporality after 1.5 or

more and less than 2.0 / in front of temporality, the viscosity ratios thing D:temporality after 2.0 or more and less than 3.0 / in front of temporality are [the viscosity ratio in front of temporality of after / temporality / the viscosity ratio thing B:temporality after less than 1.5 / in front of temporality] 3.0 or more things.[0096]Here, if it is [stability / adhesiveness, oil resistance, and / with the passage of time / viscosity] C or more ranks about B or more ranks and heat resistance, it is tolerance level practically.

[0097]The used plastic film is an OPP film (). [PAIREN P-2161 and 30 micro of film thickness] They are the Toyobo [Co., Ltd.] Co., Ltd. make, a PET film (E-5102, 12 micro of film thickness, Toyobo [Co., Ltd.] Co., Ltd. make), and a VM-PET film (VM-PET E-7075, Toyobo [Co., Ltd.] Co., Ltd. make).

[0098]

[Table 2]

表 2

		実 施 例																				
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
インキ組成(部)	顔料	30																				
	PA樹脂ワニス	20															-					
	CNワニス	20															-					
	PU樹脂ワニス	-															30					
	チタン系架橋剤75%IPA溶液	No.	1	2	3	4	5	6	7	8	9	10	11	12	1	1	1	1	2	3	1	1
		添加量	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	0.2	2.6	6.6	1.3	1.3	1.3	0.2	6.6
	混合溶剤	28.7													29.8	27.4	23.4	38.7			39.8	33.4
インキ性能	接着性	OPP	A	A	A	A	A	A	A	A	A	A	A	A	B	A	A	A	A	A	B	A
		PET	評価試験せず															A	A	A	A	A
		VM-PET	評価試験せず															A	A	A	B	A
	耐熱性		C	A	A	B	B	B	B	B	A	B	C	B	A	A	評価試験せず					
	耐油性		A	A	A	A	A	A	B	A	A	A	B	B	A	A	評価試験せず					
	経時粘度安定性		A	B	B	A	A	A	A	A	A	A	A	A	A	B	B	A	A	A	B	

[0099]

[Table 3]

表 3

		比 較 例																
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	
インキ組成(部)	顔料	30																
	PA樹脂ワニス	20									-							
	CNワニス	20									-							
	PU樹脂ワニス	-									30							
	チタン系架橋剤 75% IPA 溶液	No.	13	14	15	16	17	18	19	1	13	14	15	16	17	1		
		添加量	1.3	1.3	1.3	1.3	1.3	1.3	1.3	0.1	8.0	1.3	1.3	1.3	1.3	1.3	0.1	8.0
	混合溶剤	28.6									29.9	22.1	28.7					
インキ性能	接着性	OPP	A	A	A	A	D	A	D	D	A	A	A	A	A	D	D	A
		PET	評価試験せず									A	A	A	A	B	B	A
		VM-PET	評価試験せず									A	D	D	A	A	D	A
	耐熱性		E	A	D	A	D	A	D	E	A	評価試験せず						
	耐油性		B	A	B	A	A	A	B	D	A	評価試験せず						
	経時粘度安定性		A	D	A	D	A	D	A	A	D	D	A	A	D	A	A	D

[0100]

[Effect of the Invention]As mentioned above, as the embodiment was given and shown, the outstanding adhesiveness, heat resistance, and oil resistance are given, and the printer's ink constituent of this invention is a solvent type printer's ink constituent with good preservation stability in temporality, in order to apply to the front printing and the back printing use of a plastic film.

[Translation done.]